

## ✱Methanesulfonic Acid Catalyzed Addition of Aromatic Compounds to Oleic Acid

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### ABSTRACT

The addition of aromatic compounds to the double bond of oleic acid has been studied using methanesulfonic acid as the acid catalyst. When alkylbenzenes were reacted with oleic acid, the yield of addition product was dependent on the electron density of the benzene ring. For example, a 76% yield of addition product was obtained with toluene, whereas for benzene and monochlorobenzene, the yields of addition products were 60% and 2%. The addition of phenol to oleic acid gave 2 types of addition products, an ether-type (phenylether) product and a ring-substituted product (hydroxy-phenylstearic acid). The ratio of the 2 products varied with the reaction temperature and the amount of methanesulfonic acid. The ring-substituted product predominated at a high molar ratio of methanesulfonic acid to oleic acid (6:1) and elevated reaction temperature (50 C). Thiophenol was found to add to oleic acid to form a thioether derivative exclusively.

### INTRODUCTION

The addition of aromatic compounds to oleic acid has been studied using various types of Lewis and Bronsted acids as catalysts. Stirton (1) reported the synthesis of arylstearic acid from oleic acid by the Friedel Crafts alkylation reaction. Both sulfuric acid and a strong acid cation exchange resin were used for the addition of phenol to oleic acid by Roe (2). Later, Ault and Eisner reported that methanesulfonic acid was the preferred acid catalyst for the addition of aromatic compounds to unsaturated compounds because this acid gave not only high yields of addition products, but less colored products (3-5).

A structural study of the addition products obtained from the  $\text{AlCl}_3$  catalyzed reaction of benzene with oleic acid has been made by Smith et al. (6-10). By means of a  $\text{CrO}_3$  oxidation procedure, these workers demonstrated that the phenylstearic acid obtained was a mixture of posi-

tional isomers with the phenyl substituent located at  $\text{C}_3$  to  $\text{C}_{17}$  of the hydrocarbon chain. Although yields of the addition products have been reported, none of the by-products have been identified, so that overall, the reaction pathway has not been fully studied.

This study was undertaken to elucidate the pathway by which oleic acid reacts with aromatic compounds by identifying all of the reaction products formed when aromatic compounds are reacted with oleic acid in the presence of methanesulfonic acid.

### EXPERIMENTAL

#### Materials

Oleic acid (98%) was obtained from Applied Science Laboratories (State College, PA). Methanesulfonic acid was purchased from Fisher Chemical Company (King of Prussia, PA) and was distilled before it was used. All other reagents were used as received from commercial suppliers. Methyl esters were prepared by the boron trifluoride method (12).

Gas liquid chromatography (GLC) was conducted with a Hewlett Packard Model 7620 chromatograph equipped with dual flame ionization detectors. Separations were obtained on 8-ft  $\times$  1/8-in. silanized stainless-steel columns packed with 7.5% EGA + 2%  $\text{H}_3\text{PO}_4$  on 90/100 mesh Anakron ABS or 3% SP-2100 DOH on 100/120 Supelcoport. Thin layer chromatography (TLC) was performed on Silica gel G plates (250 micron) obtained from Analtech (Newark, DE). Plates were developed with toluene:ether (90:10) and visulalization was accomplished by spraying the plates with 50%  $\text{H}_2\text{SO}_4$  and charring. A Perkin-Elmer model 720 B infrared spectrophotometer was used for IR analyses. Mass spectra were obtained on a Hewlett Packard Model 5995 GC-MS mass spectrometer. Column chromatography was carried out on Silica gel 60 A (75-150 micron) using hexane:methylene chloride gradients as the eluant. Fractions (100 mL) from the column were monitored by TLC.

<sup>1</sup>Agricultural Research Service, US Department of Agriculture. Reference to a brand or firm name does not constitute endorsement by the USDA over others of a similar nature that are not mentioned.

## Reaction Procedure

A typical procedure is given. Oleic acid, 5 g (17.73 mmol), and benzene, 6.91 g (88.65 mmol), were placed in a 100-mL round-bottom flask equipped with thermometer, condenser, magnetic stirring bar, and addition funnel. Methanesulfonic acid, 10.21 g (106.38 mmol), was added drop by drop into the flask, stirring, at 25 C for a 10-min period, then the reaction was continued for 48 hr. Cold H<sub>2</sub>O (50 mL) was added to the flask, and the reaction products were extracted with ether (2 × 100 mL). After washing with water until the pH was ca. 7, the combined organic solution was dried over MgSO<sub>4</sub>, and the ether and benzene were removed in vacuo. The reaction products were esterified by BF<sub>3</sub>·CH<sub>3</sub>OH reagent, then separated by column chromatography. The isolated products were identified by GC, MS, TLC, and IR.

Similar reactions were carried out varying the reaction temperature, time, or molar ratio of reactants.

## RESULTS AND DISCUSSION

When benzene or an alkylbenzene, such as toluene, was reacted with oleic acid in the presence of methanesulfonic acid (Scheme 1), ring-substituted products ([3]<sup>2</sup>), and  $\gamma$  and  $\delta$  stearolactones, ([4] and [5]), were isolated as the major products. At a temperature of 25 C and a 48-hr reaction time, toluene gives 71% addition products, whereas benzene gives 46% (Table I). Higher temperature (50 C) increases the yield of addition products for both toluene and benzene, and the reactions are complete in 6 hr. Also, with benzene, an increase in alkylbenzene products is observed, as well as decrease in total lactone formation (Table I). When toluene was added to the double bond of oleic acid, the IR spectrum of product [3] shows the orientation of methyl group position ordering: para > ortho > meta. When monochlorobenzene, a deactivated

<sup>2</sup> Bracketed numbers refer to numbers in tables.

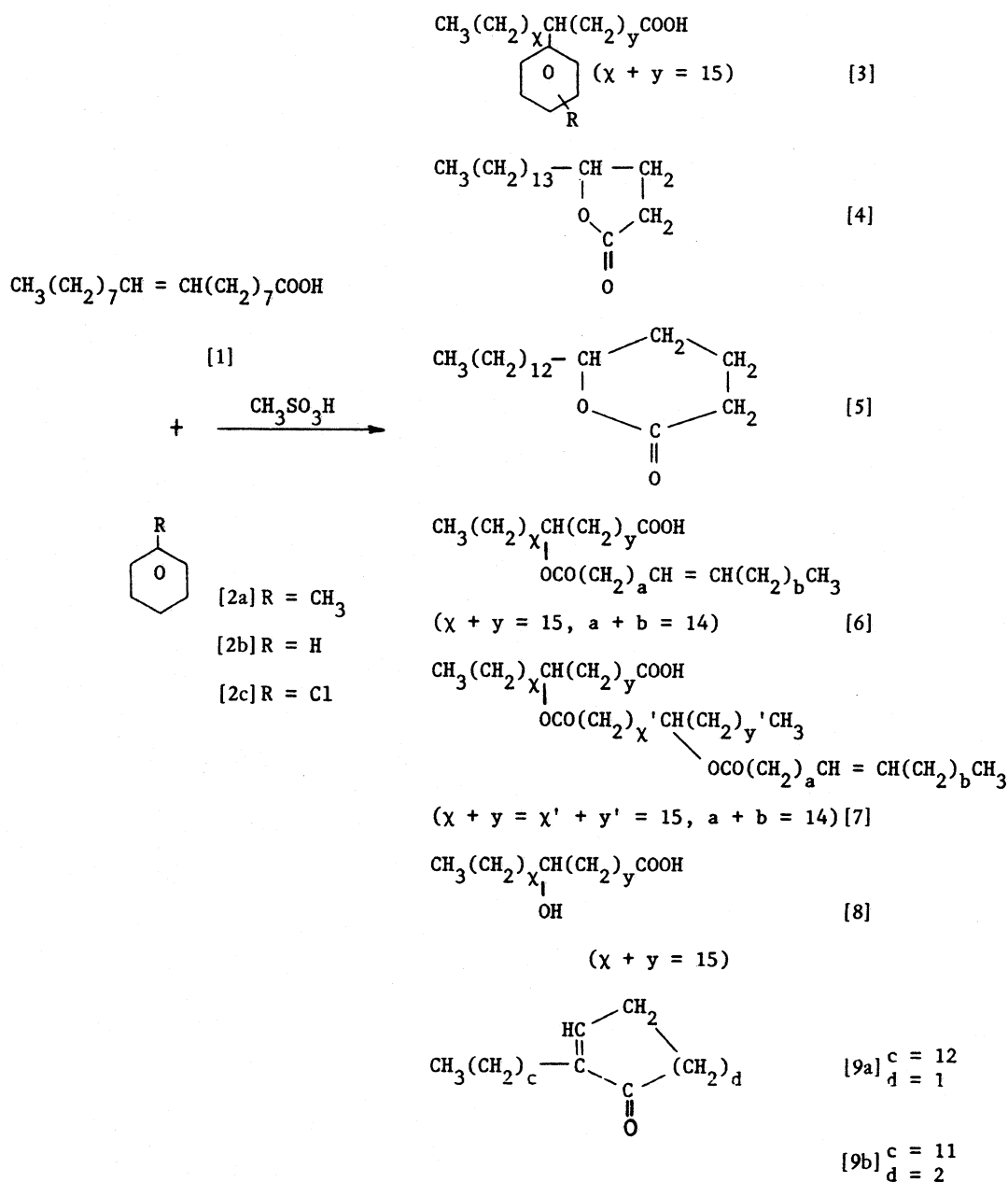


TABLE I

Reaction of Oleic Acid with Alkylbenzene  $C_6H_5R^a$ 

R	Temperature (C)	Time (hr)	Phenylstearate 3 (%)	$\gamma$ -Stearolactone 4 (%)	$\gamma$ -Stearolactone 5 (%)	6+7 (%)	8 (%)	9a + 9b (%)
CH <sub>3</sub>	25	48 <sup>b</sup>	71	4	14	5	1	4
CH <sub>3</sub>	50	6 <sup>b</sup>	76	6	9	2	1	5
H	25	48 <sup>c</sup>	46	7	25	11	3	5
H	50	6 <sup>c</sup>	59	9	17	4	2	6
Cl	50	6 <sup>d</sup>	2	15	35	10	9	9

<sup>a</sup>Oleic acid:  $C_6H_5R:CH_3SO_3H = 1:5:6$  (molar ratio).<sup>b</sup>Conversion 99%.<sup>c</sup>Conversion 97%.<sup>d</sup>Conversion 80%.<sup>e</sup>Yields recovered from column chromatography were based on oleic acid.

aromatic compound toward electrophilic substitution, was used in this reaction, only 2% ring-addition product was obtained and 50% lactone was formed. This result confirms that the addition reaction is strongly dependent on the electron density of the aromatic ring.

The initial step of the reaction is protonation of the double bond of oleic acid by methanesulfonic acid to give an alkyl carbonium ion. The latter may attack the aromatic ring to give the alkylbenzene derivative or undergo internal cyclization to give lactone derivatives after the migration of the carbonium ion along the hydrocarbon chain.

As Showell reported [11], dimer [6] and trimer [7] seemed to form by the reaction of oleic acid with carbonium ion. Similarly, cyclic ketones ([9a] and [9b]) could be formed through the protonation of the carboxyl group of oleic acid to give an acylium ion, followed by an intramolecular cyclization.

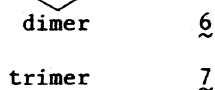
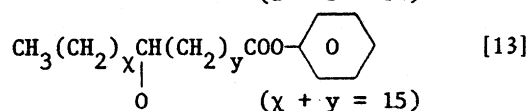
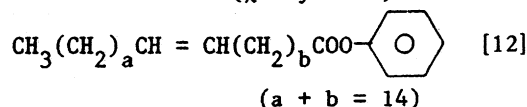
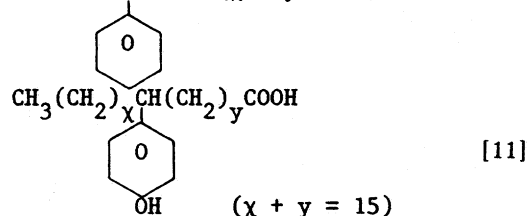
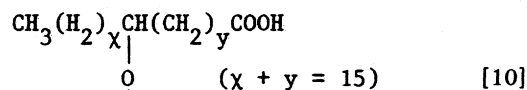
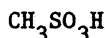
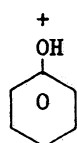
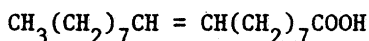
When phenol was reacted with oleic acid in the presence of methanesulfonic acid (Scheme 2), 2 types of addition products, phenylether [10] and hydroxyphenylstearic acid [11], were obtained as the major products. The yields of these 2 types of products varied with the reaction temperature and the amount of methanesulfonic acid employed (Table II). Phenol esters [12] or [13] and dimer [6] and

trimer [7] of oleic acid were formed as the minor products. Unlike with the toluene or benzene reactions, no lactones were detected.

As shown in Table II, phenylether [10] formed favorably over hydroxyphenylstearic acid [11] when low molar amounts of methanesulfonic acid were used. For example, 46% of [10] and 7% of [11] were obtained at a 1:1 molar ratio of methanesulfonic acid to oleic acid at 25 C, whereas, at a 6:1 molar ratio, an 88% yield of [11] was obtained.

The yield variation between [10] and [11] with the reaction temperature was observed particularly when methanesulfonic acid was employed with oleic acid at a molar ratio of 2:1. The phenylether [10] was formed favorably over hydroxyphenylstearic acid [11] (54% [10], 17% [11]) at 25 C, whereas yields were reversed (1% [10], 82% [11]) at 50 C (Table II).

Hydroxyphenylstearic acids [11] were the predominant form (88% [11], 2% [10]) even at 25 C, when large amounts of methanesulfonic acid were employed, such as 6:1. The formation of dimer and trimer of oleic acid ([6] and [7]) was increased by the temperature or the amount of methanesulfonic acid. Unlike the toluene reaction, orthosubstituted addition products were formed in preference to parasubstituted products, with a ratio of



Scheme 2

### Reaction of Oleic Acid with Phenol<sup>a</sup>

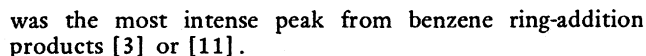
<sup>a</sup>Time 6 hr, oleic acid:C<sub>6</sub>H<sub>5</sub>OH = 1:5 (molar ratio).<sup>b</sup>Ortho:para  $\sim 4:1$ .<sup>c</sup>Yields were based on oleic acid.

When phenol was reacted with oleic acid in the presence of methanesulfonic acid at a molar ratio of 2:1:6, the reaction mixture was analyzed periodically by GLC and TLC. We found that phenylether [10] formed faster than hydroxyphenylstearic acid [11] in the initial reaction stage (30 min), then [10] decreased gradually. Hydroxyphenylstearic acid forms slowly in the early stages; then the yield increases to over 80% after a 4-hr reaction time. These results suggest as reported by others (4), that hydroxyphenylstearic acid might be formed by the rearrangement of the phenyl ether.

At a 1 to 5 molar ratio of phenylether [10] to methanesulfonic acid, 90% of the phenylether rapidly decomposed to phenol and methyl octadecenoate in less than 30 min, and hydroxyphenyloctadecenoate [11] formed gradually.

As shown in Scheme 3, unlike phenol, thioether [14] was the only addition product obtained when thiophenol was reacted with oleic acid in the presence of methanesulfonic acid. In this instance, the addition reaction was so

Mass spectra of these aromatic addition products to oleic acid clearly showed the structural difference between benzene ring-addition type products and phenylether-type products. Phenol and thiophenol were the most intense ion fragment peaks from phenylether [10] or thioether [14], whereas substituted benzyl cation



Walter I. Kimoto and Calvin J. Dooley operated GC-MS and MS, and Theodore Perlstein provided helpful discussion.

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